



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
Docket No. 12329US03

In the Application of:

ROGER BERNARDS, HECTOR
GONZALEZ, AL KUCERA and
MIKE SCHANHAAR

U.S. Serial No.: 10/028,955

Filed: December 18, 2001

For: METHOD FOR ROUGHENING
COPPER SURFACES FOR
BONDING TO SUBSTRATES

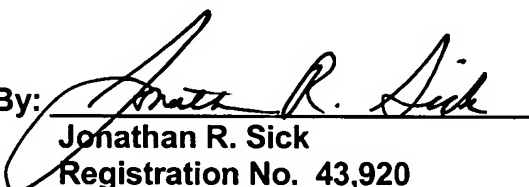
Examiner: S. Ahmed

Group Art Unit: 1765

CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Postal Service as first class mail, postage prepaid, in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on this 5th day of October, 2005.

By:


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DECLARATION UNDER 37 C.F.R. § 1.131

Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Sir:

We, Roger Bernards, Hector Gonzalez, Al Kucera, and Mike Schanhaar, declare the following:

1. We are the applicants of the above-identified patent application and coinventors of the subject matter described and claimed therein.

2. Prior to the effective filing date of United States Patent No. 6,106,899 ("Nakagawa"), which is July 16, 1998, we reduced to practice the idea of a process for preparing roughened copper surfaces comprising the steps of contacting with a clean copper surface an adhesion promoting composition under conditions effective to provide

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a roughened copper surface, wherein the adhesion promoting composition consists essentially of hydrogen peroxide, a pH adjuster, a topography modifier, and a uniformity enhancer, and at least essentially free of halogen ions.

3. Prior to the effective filing date of Nakagawa, we completed our invention as described and claimed in at least claim 1 of the present application, as evidenced by the laboratory notebook pages attached as Exhibit A.

4. The laboratory notebook pages are those of one of the undersigned applicants, Roger Bernards.

5. The first page (laboratory notebook page 29) describes the commencement of a multi-day experiment designed to develop a process for preparing roughened copper surfaces.

6. As shown on this page, a standard bath was used for each set of runs in the experiment. The standard bath contained:

- (a) H_2O_2 (hydrogen peroxide),
- (b) H_2SO_4 (sulfuric acid), and
- (c) CuSO_4 (copper sulfate).

7. The run "sets" that follow on the first and subsequent pages describe additional components that were added to the standard bath prior to applying the composition to a copper surface.

8. Set "K" is described on page 34. The heading for Set K indicates the component that was added to the standard bath for this set of runs: "5 Amino Tetrazole • H_2O ".

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9. Set K consists of 13 runs. Each run lists the concentration of 5-aminotetrazole added to the standard bath, plus any additional components that were added. Run 4 lists: ".5 g/L + 1.5 g/L BTA". BTA is an acronym for benzotriazole. In run 4, therefore, 0.5 g/L of 5-aminotetrazole and 1.5 g/L of benzotriazole were added to the standard bath.

10. Thus, the composition used in Run 4 of Set K contained the following components:

- (a) hydrogen peroxide,
- (b) a pH adjuster (sulfuric acid),
- (c) a topography modifier (benzotriazole),
- (d) a uniformity enhancer (5-aminotetrazole), and
- (e) copper sulfate.

11. As explained on laboratory notebook page 34, the composition of Run 4 was successful when applied to a copper surface: "Dark and very uniform looks great" and "What's awesome about #4 and #9 and others on this page is that no matter how [expletive] the surface is before going into the etch you get complete coverage with no skip etch."

12. Each of the dates deleted from Exhibit A is prior to the effective filing date of Nakagawa.

13. All of the work described above in paragraphs 2-11 (which is documented in the laboratory notebook pages attached to this declaration) was performed and completed in the United States of America.

14. We certify that all statements made herein of our own knowledge are true, and that all statements made herein on information and belief are believed to be true. We understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.


Roger Bernards

9/12/05
Date


Hector Gonzalez

9/27/05
Date


Al Kucera

9/9/05
Date


Mike Schanhaar

9-12-05
Date

objective To make a dark coating with Cobra bond + additives other than BTA

Standard Bath: H_2O_2 : 3% Temp 98°F (From 5% H_2SO_4 add)
 H_2SO_4 : 5% 94°F - 97°F
 $CuSO_4 \cdot 5H_2O$: 40 g/L
 Cl^- : Zero unless listed
 Additive: Variable

3-X Set A: Cobrated 928 - Material only 90% active (not taken into account for g/L)

		Gross	Tare	Dwell (min)	Etch	Appearance
{ 1)	1 g/L	1.5870	1.5159	1:10	80.5	Slightly darkened
{ 2)	3 g/L	1.5916	1.5326	1	67	Lighter but cool looking
{ 3)	5 g/L	1.5671	1.5165	1	57	same
{ 4)	7 g/L	1.5607	1.5148	1	52	same
{ 5)	10 g/L	1.5372	1.4891	1	54	same
{ 6)	15 g/L	1.6355	1.5866	1	55	maybe not as rough
{ 7)	25 g/L	1.6315	1.5857	1	52	maybe not as rough
{ 8)	0.5 g/L	1.5764	1.5172	1	67	not as rough looking

3-X SET B Cobrated P.T. (The P.T. solution has 10% H_2SO_4)

{ 1)	total 0 g/L	1.5997	1.5328	1	76	looks very smooth
{ 2)	1 g/L (active material)	1.5956	1.5520	1	49	Striations on top side Bottom side looks not etched
{ 3)	2 g/L					
{ 4)	2 g/L Repeat	1.6062	1.5338	1:20	82	Striations
{ 5)	2 g/L + 5 g/L Cl^-	1.6068	1.5995	1:20	83	No etch
{ 6)	3 g/L	1.5963	1.5225	1:20	84	Striations Big time
{ 7)	4 g/L	?	1.5388	1:28	80	Striations
{ 8)	4 g/L	1.5921	1.5288	1:20	72	"
{ 9)	5 g/L	1.6065	1.5355	1:20	80	"
{ 10)	7 g/L	1.5990	1.4924	1:20	121	"
{ 10)	10 g/L	1.5701	1.5211	1:00	55	"
{ 11)	15 g/L adjusted for H_2SO_4	1.5791	1.4745	1:50	118	"
{ 12)	1.5 g/L	1.6021	1.5327	1:20	90	Nonuniform thin marker
{ 13)	2.5	1.5961	1.5071	1:20	101	Striations Fat marker

Cont. pg 30

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RB

From pg 29

10.01

3 X Set C

TT 100 (Cobroder TT100)

	Gross	Tare	Total Etch	Dwell	Appearance
1) 0g/L	1.5813	1.4838	110	1:25	dull copper
2) 1g/L 3b/L	1.5981	1.5061	104	1:20	
3) 1g/L	1.5982	1.4978	114	1:20	
4) 2g/L	1.5988	1.5112	91	1:20	
5) 3g/L	1.5958	1.5083	99	1:20	
6) 4g/L	1.5915	1.4560	108	1:23	
7) 6g/L	1.5454	1.4644	92	1:20	
8) 10g/L	1.5770				

6 X Set D Alpha prep PC 7042 7042

1) 50% + 3% H_2O_2	1.5907	1.5660	28	1:20	look oxidized
2) " + 6% H_2O_2	1.5787	1.5352	49	1:20	striations
3) " + 9% H_2O_2	1.6033	1.5281	85	1:20	BTA on surface
4) " + 9% H_2O_2 + 4.3.9% H_2SO_4 (50% total)	1.5909	1.5025	100	1:20	striations
5) " + 9% H_2O_2 + 3.9% H_2SO_4 + 13.5g/L $CuSO_4 \cdot 5H_2O$	1.5770	1.4993	88	1:30	Bath turned green

6 X SET E NaBr at 8.5g/L BTA

1) 4.5g/L 3% H_2O_2	1.5857	1.5776		1:20	
2) " 6% H_2O_2	1.5956	1.5843	13	1:20	
3) " 9% H_2O_2	1.6040	1.5852	21	1:20	Looks like cobalt et
4) " + 12% H_2O_2	1.5867	1.4727	129	1:20	Looks like Cobra w. Cl ⁻ stained
5) 1.2g/L 14% H_2O_2	1.5826 1.5935 1.6149	1.5348	91	1:20	Cont. on pg 32

UNRENDERED AND UNRENDERED

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R.B.

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6) 0.5351L NaBr
+ 14% H_2O_2
+ 8.531L BTA

1.5739 1.5138

68 1120

Stained like oil

~~Glicont F-1~~ ~~1.5879 1.5878~~
~~+ 5% H_2SO_4~~
~~+ 3% H_2O_2~~

SET F Glicont F-1 Lot 961205 exp [REDACTED]

Normal conditions i.e. 5% H_2SO_4 + 3% H_2O_2 + 40g/L $CaSO_4 \cdot 5H_2O$ 198°F

25% by Vol F-1 1.5872 1.5866 0.7 1:30 Bright water beads up on it

25% + 9% H_2O_2 1.6080 1.6076 still no etch "

10% + 3% H_2O_2 1.6049 1.6040

20% + 14% H_2O_2 1.6191 1.6140 6 2:00 still no etch

2% + 3% H_2O_2 1.5761 1.5698 7 1:20

2% + 14% H_2O_2 1.5752 1.5443 35 1:20 still Bright but not as shiny

Part gasses like crazy
but still hardly no etch
 H_2O_2 Breaking down by
side Rx

6X → SET G Glicont E2L

2% + 3% H_2O_2 1.5728 1.5446 32 1:20

Bright but not shiny

2% + 6% H_2O_2 1.6035 1.5034 112 ± 2:00

Bright but not shiny

Part really gassing no not much etch

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Cont. Pg 33

2 X SET H 1-Methylimidazole normal conditions unless otherwise stated

- (1) 5g/L 1.5998 1.5803 22 1:20 Bright Shiny
- (2) 5g/L + 8.5 BTA 1.5797 1.5150 73 1:20 not as Dark as just BTA
- (3) 5g/L + ~~8.5 BTA~~ 1.5056 Fairly Dark
+ 3.0 BTA

3 X SET I 2,1,3-Benzothiadiazole

- (1) 5g/L 1.6117 1.5537 66 1:30 Light
Not all dissolved looks completely insoluble
- (2) 5g/L + 3g/L BTA 1.5755 1.5043 81 1:20 Slightly Dark

3 X SET J 1H-2,1,2,3-Triazolo(4,5-b)pyridine

- (1) 5g/L 1.5982 1.5435 62 1:20 Big time striations
Looks like fire
- (2) 5g/L + 3g/L BTA 1.5900 1.5296 68 1:20 Brown
- (3) 10g/L 1.5983 1.5385 68 1:20 striations Bad
- (4) ~~1.5535 1.5383~~ 1:20 Still some striations
10g/L + 3g/L BTA
- (5) 5g/L 1.5972 1.5169 91 1:20 striations
- (6) 5g/L + 3g/L BTA 1.5748 1.4955 90 1:25 Looks like BTA only
Marker spreads

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Cont. on Pg 34

2 X BET K5 Amino Tetrazole H₂O.

- { 1) 5g/L 1.5839 1.5313 60 1:20 Light but rough
- { 2) 5g/L + 3g/L BTA 1.5744 1.5096 73 1:35 Reddish Looking
Marker spreads
- { 3) 0.5g/L — 1:20 Looks like BTA
Little lighter
- { 4) .5g/L + 1.5g/L BTA 1.4935 1.3685 142 1:50 Dark and very
uniform looks
great
- { 5) .5g/L + 3g/L BTA ~~1.4979~~ ~~1.4979~~ 1:20 Darker but not
uniform skip
- { 6) 0.25g/L 1.5798 Darker lighter fair
uniform
- { 7) .25g/L + .5g/L BTA 1.6148 1.5419 82 Lighter fairly
uniform
- { 8) .25g/L + 1g/L BTA 1.5892 1.5212 77 1:20 Kinda Dark
fairly uniform
Not uniform
- { 9) .5g + .5g BTA 1.5777 1.5046 83 1:28 Dark even
notes Dark as #4

Note: What's Awesome about #4 and #9 is that no
matter how shitty the surface is before going into the
etch you get complete coverage with no skipetch
and others on this page

- { 10) .5g/L + 1g/L BTA 1.6180 1.5552 71 1:20 Dark even, notes
Dark as 4
- { 11) 1g/L + 1g/L BTA 1.5845 1.5280 64 1:20 Down side is
darker than up
notes Dark as 10
- { 12) 1g/L + 2g/L BTA 1.6051 1.5348 80 1:27 Dark uniform
complete coverage
- { 13) 1g/L + 3g/L BTA 1.6103 1.5432 76 1:21

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Continued pg 34

WITNESSED AND UNDERSTOOD

SIGNED

John [unclear]

DATE

[redacted]

SIGNED

RB

[redacted]

DATE

DATE

The main conclusion drawn from the testing of the many additives from pages 27-47 can be found on pg 34. From ~~Set K~~ ^(Set K) ~~The~~, see the note entered on that page. The 5 Amino tetrazole acts as a uniformity enhancer if it is in the right concentration and if it is in the right ratio with the BTA. This is a big improvement over the BTA only system and may be patentable. Further testing by others & at electrochemicals [see Al Kucera's, Hector Gonzales' and Mike Schanhaar's Notebooks] Also show that the 5 amino tetrazole acts as a uniformity enhancer. i.e. the panels look more uniform in color, degree of etch, ^{and} coverage of the coating when the 5 amino tetrazole is used in conjunction with the BTA. Also the 5 amino tetrazole when used as the sole additive is not as uniform as when used in conjunction with the BTA. On pg 34 #4 is definitely better than #1 as ~~was~~ was noted when I said wrote #4 "looks great." The optimum Ratio of BTA to 5 amino tetrazole is close to 3 to 1 and the best concentration of BTA is close to 1.5g/L and the best concentration for 5 amino tetrazole is ^{close to} 0.5g/L. The H_2O_2 , H_2SO_4 , Temp., Copper (Copper can be zero, Copper is not needed to make this formulation work properly), Concentration concentrations can vary a lot but I think H_2O_2 = .2% - 5%, H_2SO_4 .1% - 8%, and Temp 60°F - 130°F is the best range. Most commonly H_2O_2 = 1% - 2%, H_2SO_4 4-6%, and Temp 80-100°F is employed.

Rogn Bur

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Lee Bright

RIB